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Nanostructured (Bio)sensors for smart agriculture

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ABSTRACT

Intense farming represents one of the main sources causing detriments to vital resources as lands and water, due to unsustainable agricultural practices and the resulting environmental pollution. Furthermore, the increasing world population and the impact of climate change contribute to worsen these constraints. To these regards, several attempts have been completed to provide pioneering technologies for facing against these challenges, including nanostructured (bio)sensors. Indeed, nanotechnology-based (bio)sensors, thanks to the exploitation of fascinating properties of functional materials at the nanoscale, can support farmers in delivering fast, accurate, cost-effective, and in field analyses of i) soil humidity, ii) water and soil nutrients/pesticides, and iii) plant pathogens. Herein, we report a glance of the nano nanostructured (bio)sensors developed to support smart agriculture, reporting representative examples form the literature of the last 10 years.

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1. Introduction

The increasing demographic pressure, the climate change, and the enhanced competition for resources of the last decades made the challenge of guaranteeing suitable food worldwide even harder. To meet this requirement, farming practices have been oriented towards the indiscriminate use of resources, high-tech machinery, and chemicals for producing massive food volumes. However, this caused an abuse of soil and water, while triggering huge pollution levels in different environments and affecting human/animal well-being. As an example, according to the Bulletin of the World Health Organization (WHO), more than 26 million human pesticide poisonings with about 220.000 deaths occur per year worldwide [1]. Furthermore, agricultural production is responsible for 85% of global water consumption [2], becoming severely associated with negative environmental and economic impacts. Also, as highlighted by the Food and Agriculture Organization of the United Nations, the arable lands per person expressed as hectares are been falling for 50 years because of the abuse of resources for farming applications [3].

The endangering effects of intense agriculture on the ecosystems have turned significant worries amongst environmentalists, encouraging green policies towards more sustainable farming approaches. In 1992, the United Nations Framework Convention on Climate Change (UNFCCC) commissioned a reduction of greenhouse gas emissions with the aim of stabilizing their concentrations in the atmosphere and thus not distressing the climate system [4]. Afterward, several international agreements have been drafted, including the Kyoto Protocol in 1997 and the Conference of Paris in 2015, for limiting global warming to less than 2 °C (3.6 °F) compared to pre-industrial levels.

In this context, the adoption of more sustainable agricultural practices based on a wise usage of resources without generating detriment of ecosystems become crucial. Smart agriculture involves multifarious approaches based on more energy-efficient and environmentally friendly cross-cutting technologies, including: i) nanoformulation delivery systems to improve dispersion and wettability of nutrients/pesticides, ii) sensors for fertiliser/pesticide residue analysis of soil and crop, and iii) remote sensing, yield mapping, and positioning systems for crop growth/disease control [5]. Among these technologies, nanostructured (bio)sensors are gaining momentum, being able to evaluate crop maturity and status health, detect and tune the amount of fertilisers and pesticides, and sense soil humidity to tailor irrigation avoiding water misuse.

Nanostructured (bio)sensors exploit the fascinating features of nanomaterials for different purposes, such as i) the functionalisation and the immobilisation of the bioreceptor on a transducer to

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Table 1
Nanostructured biosensors applied for agricultural real sample analysis.

Target analyte	Sensing strategy	Transduction	Nanomaterial exploited	LOD	Analysis time	Pre-treatment	Ref.
Atrazine in soil	Inhibition of tyrosinase	Amperometric analysis using conventional 3 electrode cell	TiO_2 nanotubes	0.1 ppt	ca. 10 min	Long procedure (more than 48 h) requiring laboratory set-up	[17]
Methyl parathion in water and soil	Inhibition of AChE	Differential pulse voltammetry using modified glassy carbon electrode	Multi-walled carbon nanotubes-chitosan nanocomposite	7.5×10^{-13} M	2 s	Long procedure (more than 24 h) requiring laboratory set-up	[18]
Acetamiprid in soil	Affinity with 20mer specific aptamer	Colourimetric analysis	Gold nanoparticles	5 nM	5 min	Long procedure (more than 48 h) requiring laboratory set-up	[19]
Glyphosate and glufosinate in soil	Specific double-template imprinted polymers	Differential pulse anodic stripping voltammetry using gold nanoparticle modified pencil graphite electrode	Multiwalled carbon nanotubes	0.35 ng mL^{-1} 0.19 ng mL^{-1}	Few min	Short and simple in field procedure	[20]
Nitrate in soil	Solid state ion selective electrode of polypyrrole	Potentiometric analysis using modified glass carbon electrode	Graphene oxide	10^{-5} M	≤15 s	Short and simple in field procedure	[23]
Nitrate in soil	Nitrate reductase	Impedimetric analysis using gold electrode	PEDOT nanofibers -graphene oxide nanosheets composite	0.68 mg/L	Few min	Long procedure requiring laboratory set-up	[24]
Urea and urease activity in soil	Gold nanoparticles acting as a catalyst imitating horseradish peroxidase	Colourimetric pH indicator	Gold nanoparticles	5 μM 1.8 U/L	10 min	Short and simple in field procedure	[25]
Synthetic DNA of *Ganoderma boninense*	DNA probe	Fluorescence resonance energy transfer	Quantum dots	3.55×10^{-9} M	10 min	n.d.	[32]
Pantoea stewartii sbusp. *stewartii*-NCPPB 449 in corn seed soak	Immuno-sensor	Enzyme-linked immunosorbent assay (ELISA)	Gold nanoparticles	7.8×10^{3} cfu/mL	Less than 30 min	n.d.	[34]
Cymbidium mosaic virus *Odontoglossum ringspot* virus in orchids	Fibre optic particle plasmon resonance	Immunosensor using gold nanorods as sensing materials	Gold nanorods	48 pg/mL 42 pg/mL	10 min	Direct analysis without pre-treatment procedure	[35]
Trichoderma harzianum in soil	Single-stranded DNA probe	Electrochemical analysis using gold electrode	ZnO nanoparticles-chitosan nanocomposite membrane	1.0×10^{-19} mol/L	10 min	Long procedure for DNA extraction requiring laboratory set-up	[38]

dramatically improve its analytical performances, as well as ii) the miniaturisation and integration of biocomponents, transduction systems, electronics and microfluidics in complex architectures [6,7]. Nano(bio)sensor technology can foster more sustainable approaches to assist the management of agricultural practices by furnishing a comprehensive and early picture of the status of the resources (water and land) as well as chemicals (fertiliser and pesticides), with the potential to rapidly tailor intervention decisions and enhance crop yields respecting ecosystems. The aim of this review is to provide an overview of the nanostructured (bio) sensors developed for the agricultural sector, with a special focus on sensing systems for the detection of pesticide/nutrients residues, plant pathogens, and soil humidity. The nanotechnology based (bio)sensors applied to analyse real samples as soil and plants were reported in Table 1, highlighting their main features in terms of target analyte, analysed matrix and its pre-treatment procedures, sensing strategy, transduction system, nanomaterial exploited, limit of detection (LOD), and analysis time.

2. Discussion

2.1. Nanostructured (bio)sensors to detect soil pesticides

In the last decades, the enlarged uses of pesticides have become compulsory to maximise the agricultural productivity and thus to face the increasing food demand due to population rising. Among pesticides, atrazine and glyphosate are the most widely used herbicides according to data from the USDA National Agricultural Statistics Service (NASS), probably due to the intensification in resistant weeds [8]. Although their helpful role in agriculture, pesticides are hazardous compounds affecting human, non-targeted organism, and ecosystem health [9]. For this reason, pesticide detection through nanostructured (bio)sensors become helpful to foster healthy agriculture. Pesticide monitoring in agriculture is challenging and requires cutting-edge technologies, especially regarding their discrimination in complex agricultural matrices such as soil, water, and crop. Compared with conventional methods and last generation (bio)sensors, nanomaterial based (bio) sensors have great advantages such as: high sensitivity due to high surface-to-volume ratio; fast response time; ability to mediate fast electron-transfer kinetics; highly stability and longer lifetime [10].

A huge number of nanostructured (bio)sensors have been realised for pesticide detection in water and food exploiting different types of nanomaterials, including carbon nanotubes [11], quantum dots [12], gold nanoparticles [13], Prussian Blue nanoparticles [14], carbon black [15], and nanocomposites [16]. However, soil analysis represents the essential task in agriculture but arduous due to soil ability to retain chemicals as pesticides as well as the low homogeneity, thus requiring pre-treatment procedures and a multiple sampling. Nanostructured (bio)sensors can overcome these

challenges thanks to their ability to operate in complex matrices avoiding sophisticated treatment procedures as well as to perform fast analysis allowing multiple measurements. To report an example, a tyrosinase/TiO_2 nanotubes based biosensor was developed by Yu and colleagues [17] for atrazine detection in soil in the ppt range. A tubular structure was fabricated by vertically growing TiO_2 nanotubes to obtain highly ordered vertically aligned nanotubes able to provide a large surface area for the immobilisation of tyrosinase enzyme (Fig. 1A). This structure allowed for a good enzyme loading and electron transfer resulting in a higher sensitivity and robustness of the system. The nanobiosensor was also challenged in soil samples. In detail, paddy soils were collected at different depths, air-dried, ground with a pestle and mortar, sieved with a 1.0 mm filter, dried again in a vacuum oven at 35 °C for 48 h, solubilised with acetone and shaken at 25 °C for 1 h; thus, supernatants were analysed and atrazine detected in a wide detection range from 0.2 ppt to 2 part-per-billion (ppb), with a standard deviation less than 5% when compared with HPLC data.

Dong and colleagues [18] described a nanobiosensor for ultra-trace detection of pesticides in water and soil by immobilizing acetylcholinesterase enzyme on multi-walled carbon nanotubes-chitosan nanocomposites modified glassy carbon electrode (Fig. 1B). Methyl parathion was quantified analysing its inhibitory effect on AChE enzyme using 5,5-dithiobis (2-nitrobenzoic) acid (DTNB) as electrochemical mediator, in a concentration range between 1.0×10^{-12} and 5.0×10^{-7} M and a detection limit of 7.5×10^{-13} M. Moreover, the practicality of the proposed nanobiosensor was further confirmed by means of recovery tests on spiked soil samples, after a simple pre-treatment, with recoveries from 93.8% to 103.2%. In particular, water samples from Naihe River (Shandong, China) were filtered with a 0.45 μm filter to eliminate particulate matters and the pH was adjusted to 7.0; while soil samples from trial plots of Shandong Agricultural University (China) were homogenized, sieved (2-mm mesh), and air-dried at room temperature. After, methyl parathion was extracted with ethanol in an ultrasonic bath for 30 min, followed by centrifugation, collection of supernatant and dilution with phosphate buffer.

Shi et al. (2013) [19] developed a colourimetric nanobiosensor for the detection of acetamiprid in soil combining the amazing properties of nanomaterials with the incredible features of artificial molecules, which show important advantages with respect to natural one in terms of higher stability, selectivity, and sensitivity (Fig. 1C). In particular, the authors designed by SELEX a novel 20mer acetamiprid-binding aptamer functionalised with gold nanoparticles to optically detect acetamiprid within a linear range between 75 nM and 7.5 μM. The proposed colourimetric method was applied in soil from the field in Tongji University in Shanghai (China). Soil samples were air-dried, ground to pass in a 1.0 mm sieve, and again dried in a vacuum oven at 35 °C for 48 h; then, CH_2Cl_2 was added to samples thus ultrasonically extracted and finally filtered.

Following a similar route, Prasad et al. [20] designed a novel artificial molecule able of recognising phosphorus-containing amino acid-type herbicides in soil (Fig. 1D). In detail, a double-template imprinted polymer was synthesized and immobilised on a nanofilm-modified pencil graphite electrode for the simultaneous analysis of glyphosate and glufosinate by pulse anodic stripping voltammetry. This sensor observed wide linear ranges (3.98–176.23 ng mL^{-1} and 0.54–3.96 ng mL^{-1}) with detection limits of 0.35 and 0.19 ng mL^{-1} (S/N = 3) for glyphosate and glufosinate, respectively, in aqueous samples. Soil samples from a local agricultural land were also analysed after suspension in water (1.0 g/30 mL) and removal of solid residues by centrifugation and filtration, with recovery values of 98.6 and 102.8%.

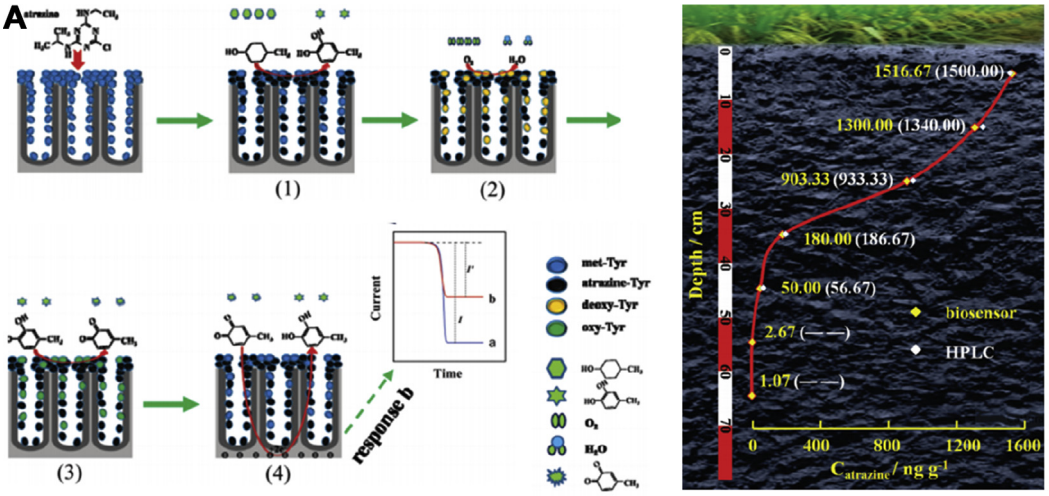
2.2. Nanostructured (bio)sensors to detect nutrients

According to the FAOSTAT, fertiliser consumption is increasingly growing worldwide [3]. The use of fertilisers in agriculture has the main purpose of enhancing productivity promoting plant growth and potent stimulation of soil life [21]. Nonetheless, fertilisers have significant environmental implications being able to pollute surface and groundwaters when spread into the environment. Furthermore, since industrial wastes can be exploited as fertilizers but they may also enclose heavy metals (e.g. lead, arsenic, and cadmium), they can affect environmental health. To this regard, reasoned fertilization is demanded through the application of nutrients in correct weather conditions, at the appropriate stage in crop growth, and at the right doses. This can be accomplished through a comprehensive and accurate analysis of fertilizers in soil and water to better adapt their usage. Conventional soil sample analyses for fertilisers are expensive and time-consuming if applied through a temporal-spatial strategy as compulsory in precision agriculture; in addition, fertilise analysis in soil is arduous being also these compounds retained in soil. In this context, nanostructured (bio)sensors can foster more sustainable practises by accurate monitoring fertilisers in water and soil, and thus supporting farmers to obtain information about spatial and temporal variations of fertiliser concentrations within the field. Indeed, sensors showed in the last years their high potential to evaluate soil organic matter or total carbon content, soil salinity, sodium content, residual nitrate, phosphate, and urea.

However, their use is still restricted to analysis in standard solutions and water samples, while very few examples of nanostructured (bio)sensors have been applied for soil analysis. As an example, nitrate detection in water has been described by Mura et al. [22] through a colourimetric assay developed using cysteamine modified gold nanoparticles (Fig. 2A). These nanoparticles modified with cysteamine were able to capture nitrates with excellent affinity and quantify them by naked eye colour variations within a concentration of 35 ppm. The authors performed in field analysis in underground water extracted from wells in Arborea area (Italy), a nitrate vulnerable zone, without the need for sample pre-treatment and obtaining excellent results.

Similarly, Pan et al. [23] realised a solid state sensor for soil nitrate detection using polypyrrole doped with nitrate (PPy-NO_3^-) as the ion-selective membrane (Fig. 2B). They firstly introduced a graphene layer as a hydrophobic solid contact layer by electrochemical reduction of graphene oxide onto the surface of glass carbon electrode. Then, they immobilised a PPy-NO_3^- film on the graphene layer by a pulsed electro-polymerization technique. The proposed nanosensor demonstrated the ability of graphene layer to restrain the water layer formation and effectively promote ion-to-electron transition, significantly enhancing the stability and response rate. A wide linear range (10^{-5} - 10^{-1} M) and a short response time (≤15 s) were obtained. In addition, satisfactory results on real samples were achieved on soil samples from Beijing rural area covering high, middle, and low nitrate levels using an easy pre-treatment process: soil samples were dried at 60 °C, crashed, and sifted through a 1 mm siever, and nitrate was extracted by water dilution, shaking 15 min, and filtering with filter paper.

Nitrate detection in soil has been reported by Azahar Ali and coworkers [24] which realised a microfluidic impedimetric sensor using a graphene oxide (GO) nanosheets and poly (3,4-ethylenedioxythiophene) nanofibers (PEDOT-NFs) (Fig. 2C). The authors demonstrated the ability of PEDOT NFs-GO composite to host nitrate reductase enzyme and quantify nitrate ions in real samples extracted from soil of a *Zea mays* farm, within a wide concentration range of 0.44–442 mg/L and a detection limit of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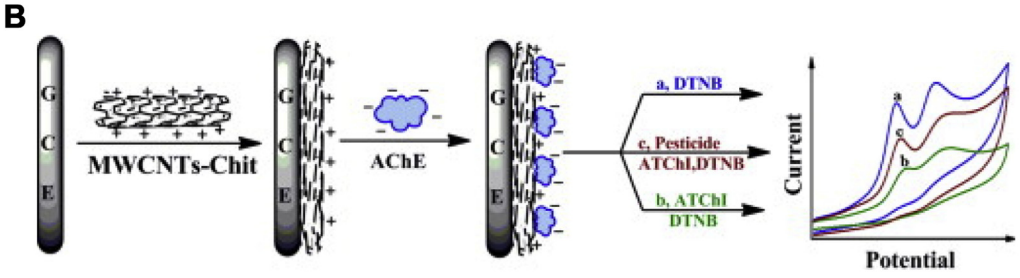
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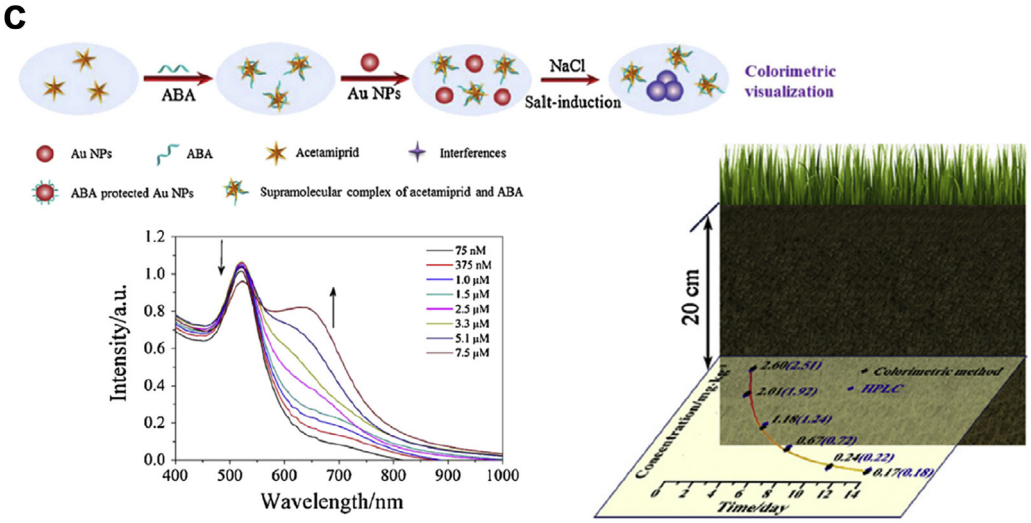
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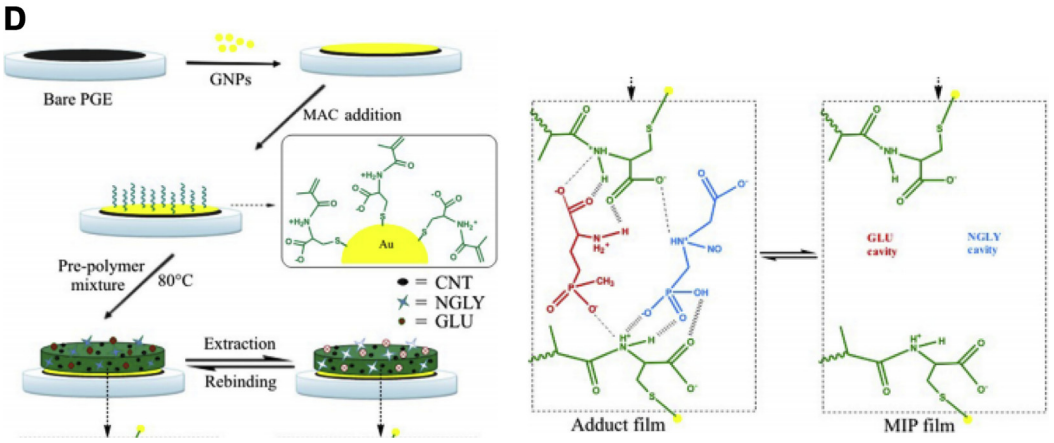
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0.135 mg/L. A very simple sample preparation was performed by drying soil at 105 °C and extracting nitrate by adding 2 M KCl solution, shaking for 1 h, and filtrating using Whatman #1 filter paper. The extracted samples were thus loaded into a syringe and infused into the device using a pumps, needles, and microfluidic tubing, obtaining brilliant detection results in terms of selectivity, stability, and reproducibility.

Urea is also largely exploited as a nitrogen fertiliser in agriculture; however, being rapidly hydrolysed to ammonium carbonate it causes many hazardous effects such as damage to germinating seedlings and young plants or nitrite toxicity. For these reasons, the availability of satisfactory methods to quantify urea in soils become essential. A considerable number of nanostructured (bio)sensors for urea detection have been reported in literature based on different nanomaterials including metal and magnetic nanoparticles, nanorods, nanotubes, nanocomposites, graphene among others. Nevertheless, these nanostructured (bio)sensors are still in early stage applications since they have been challenged only in standard solutions, or they have been realised for biomedical field and *in vitro* diagnostics. An alternative strategy is based on the assay of urease activity in soil that can be ascribed to the presence of intracellular urease of ureolytic bacteria or extracellular urease released from disrupted plants and microbial cells. Deng et al. [25] reported for the first time a colourimetric sensing system based on gold nanoparticles-catalysed 3,3′,5,5′-tetramethylbenzidine-H_2O_2 as an ultrasensitive colourimetric pH indicator with a great potential application in biosensing for urea, urease, and urease inhibitors. In detail, the gold nanoparticles acted as a catalyst imitating the function of horseradish peroxidase. The absorbance at 450 nm of the yellow-colour product in the catalytic reaction exhibited a linear fashion over the pH range of 6.40–6.60. This system (Fig. 2D) was used to detect urease with detection limit of 1.8 U/L in sand sample collected from Fujian Medical University campus. Soil samples were air-dried and crushed; known amounts of urease were added into the screened soil sample, together with phosphate buffer/2% (v/v) toluene solution; the mixture was centrifuged and the supernatant collected and purified through ultra-filtration for the analysis.

A vast number of sensors have been described also for phosphate detection [26], but they are likewise restricted to environmental applications for the analysis of river water [27], tap, river, and lake waters [28], and environmental samples [29,30].

2.3. Nanostructured (bio)sensors to monitor plant diseases

Crop productivity is daily endangered by pests, weeds, and pathogens, which affect the relative farm economy; for this reason, crops must be protected with proper actions. In this context, nanostructured (bio)sensors can provide their contribution in smart agriculture by monitoring not only soil conditions and crop growth over vast areas but also detecting infectious diseases in plants before visible symptoms occur. Several nanomaterials have been employed for the design of (bio)sensors devoted to this specific application. Quantum dots, a class of luminescent semiconductor nanocrystals with broad excitation spectra, are one of the most utilised nanomaterials. Safarpour and colleagues developed a quantum dots FRET-based biosensing system to detect *Polymyxa betae*, a vector of beet necrotic yellow vein virus responsible for Rhizomania disease in sugar beet, after plant roop sap samples pre-treatment for virus extraction [31]. Bakhori and colleagues exploited the same FRET technology for the detection of synthetic oligonucleotide of *Ganoderma boninense* (Fig. 3A), an oil palm pathogen, modifying quantum dots with carboxylic groups and conjugating them with a DNA probe, obtaining high sensitivity with a LOD of 3.55×10^{-9} M [32].

Gold nanoparticles have been also largely employed for sensor functionalisation in sensing systems for pathogen detection thanks to their high surface-to-volume ratios, offering lower detection limits and higher specificity in comparison with conventional strategies [33]. Oilseed rape samples were treated and analysed by flash-freezing in liquid nitrogen to terminate any metabolic activity, homogenising in cold water and stirring overnight; then, extract was ultrasonicated, centrifuged and adjusted to 0.2 M NaOH before electrochemical measurement. Zhao and colleagues presented an electrochemical enzyme-linked immunoassay using gold nanoparticle tags with antibodies of Horseradish peroxidase to detect *Pantoea stewartii sbusp. stewartii* plant bacterial pathogen (Fig. 3B), reaching a detection limit of 7.8×10^3 CFU/mL [34].

Gold nanorods were reported by Lin and colleagues [35] to develop a label free SPR immunosensor to monitor two viruses of orchid *Cymbidium mosaic virus* (CymMV) or *Odontoglossum ringspot virus* (ORSV), achieving LODs of 48 and 42 pg/mL for CymMV and ORSV in leaf saps, respectively, tremendously lower than LODs of 1200 pg/mL gained by ELISA. Plant crude saps were treated for real samples analysis by grinding fresh leaf with PBS solution and centrifuging to remove plant tissue; then, supernatants were diluted 25-fold with PBS solution to circumvent the undesirable signal change caused by the RI variation of bulk medium during the sensing process.

Despite nanoparticles, nanomaterials as carbon nanotubes, graphene, nanowires, and nanocomposites have widely helped the development of nanosensing platforms for the detection of pathogens and mycotoxins (Malhotra et al. 2014) providing to the farmers easy to use, fast, and portable nano-diagnostic kits in support of an effective prevention and management of epidemic diseases. Moreover, nanochannels and nanopores have also been described as smart nanomaterials for pathogens and pests sensor development [36,37]. Also, an electrochemical DNA biosensor for the identification of a soil-borne fungi *Trichoderma harzianum* and crude DNA taken from real samples was successfully developed by using a ZnO nanoparticles/chitosan nanocomposite modified gold electrode [38]. This nanobiosensing system was capable of detecting the target analyte at concentration ranges of 1.0×10^{-18} - 1.82×10^{-4} mol L^{-1}, with a LOD of 1.0×10^{-19} mol L^{-1}.

Despite the use of smart nanomaterials for the labelling and/or immobilisation of the bioreceptors on tailored supports, nanotechnology can be also helpful for the construction of nanodevices being capable of operating on the structure of the sensor systems, including microfluidics and instrumentation. In addition, nanotechnology powerfully supports the design of innovative autonomous/robotic biosensors linked into GPS system for extensive, continuous, and remote control of plant pests.

2.4. Nanosensors to detect soil humidity

Despite soil nutrients/pesticides and crop diseases, crucial parameters requiring real time and accurate analysis are soil texture, moisture, and water content (humidity), since these parameters are

Fig. 1. A) Schematic Illustration for Mechanism of the Biosensor and the found spatial distribution of atrazine in soil. B) AChE immobilised on multi-walled carbon nanotubes-chitosan nanocomposites modified glassy carbon electrode. C) Schematic illustration of the mechanism of the colourimetric detection of acetamiprid utilizing ABA and unmodified Au NPs as well as its selective performance; and the concentration changes of acetamiprid in 20 cm deep soil versus time after application. D) Schematic representation of double-template imprinted polymer-modified gold nanoparticles modified pencil graphite electrode fabrication along with suggested binding mechanism for simultaneous analysis of glyphosate and glufosinate in their respective MIP cavities.

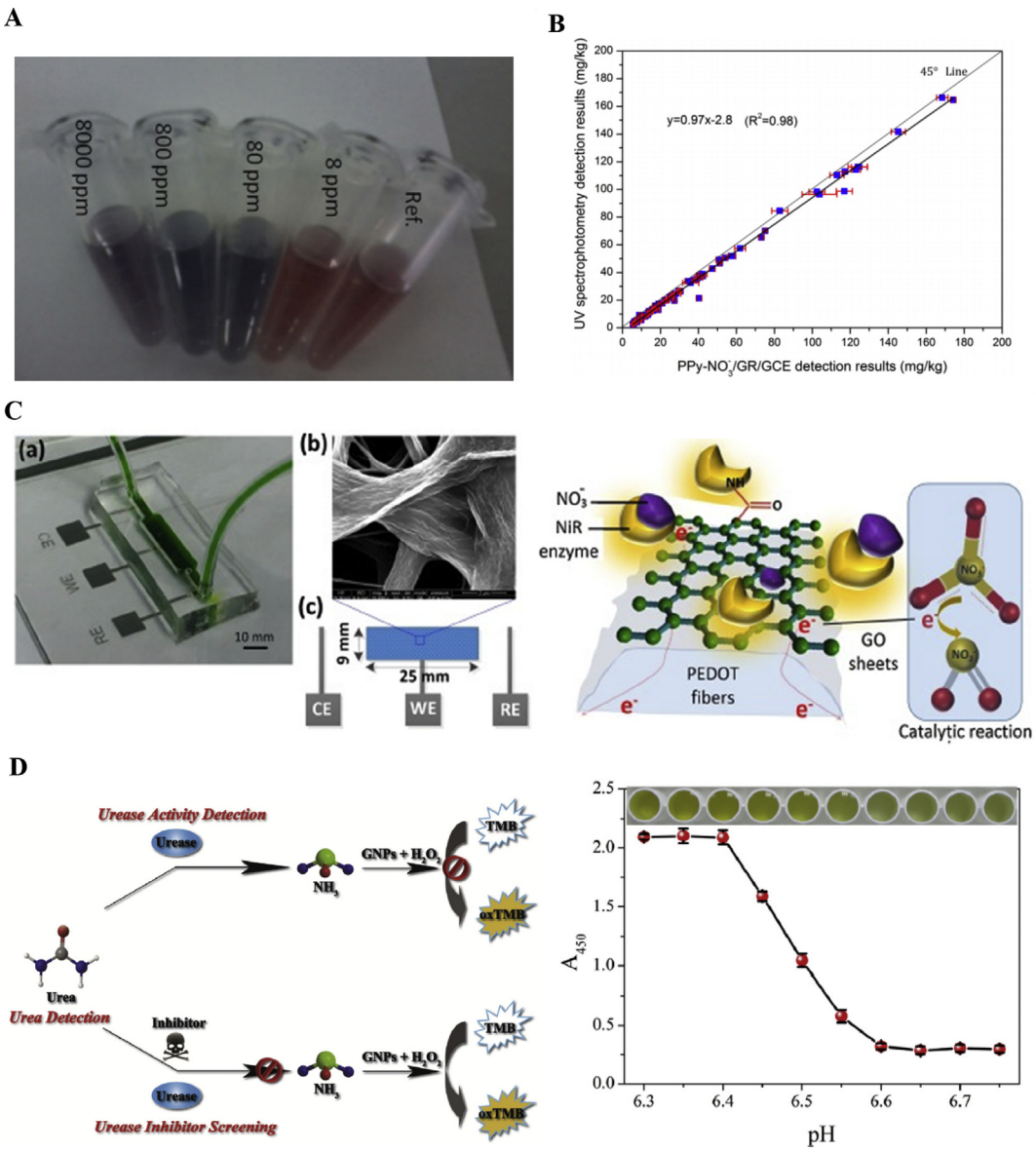

Fig. 2. A) Pictures of AuCyNPs alone and with nitrates at different concentrations (NPs boiled 3 h). B) Validation of measurement results for practical soil samples. C) Photo of the fabricated microfluidic sensor using a PEDOT NFs-GO composite to modify the working electrode for detection of nitrate ions. The channel was loaded with food dye for easy visualization (*a*). Scanning electron microscopic (SEM) image for the PEDOT NFs-GO composite (*b*). Geometry and layout of the working electrode of the sensor (*c*) and schematic of the surface immobilisation of PEDOT NFs-GO with NiR enzyme to realize electrochemical nitrate detection by catalytic conversion of nitrate to nitrite. D) Schematic illustrations of the sensing protocols for urea, urease, and urease inhibitor.

highly mutable in space and time and their spatio-temporal variations may affect agricultural yields. Conventional approaches are able to evaluate a wide range of data, but they also display several drawbacks in terms of extensive time response and labour, low accuracy, need for individual calibrations, and questionable long-term stability. In this perspective, a number of functional materials with humidity sensing properties have been discovered and exploited to design innovative sensors for agriculture applications, including quality management of the soil, environmental condition control, plant cultivation, greenhouse air-conditioning, plantation protection, soil moisture monitoring, and cereal storage.

Humidity analysis is based on the measure of amount of water vapour present in a gas mixture, such as air, that is usually expressed in relative humidity (RH), which is the ratio of the partial pressure of water vapour present in a gas to the saturation vapour pressure of the gas at a given temperature [39]. Founded on this principle, several humidity sensors have been described, mainly based on electrical transduction (impedance ionic or impedance electronic or capacitance type) [40] exploiting hygroscopic materials whose dielectric properties alter upon the absorption of water molecules. In combination with these sensors, different materials including polymers, ceramics, and composites have proven their advantages for humidity sensor application, such as chemical and thermal stability, high sensitivity, environmental adaptability, small humidity hysteresis and simple technique, and wide range of working temperature. However, investigations on the synthesis of novel materials are still required, thus many efforts have been spent to provide novel materials with improved features in terms of sensitivity, repeatability, response/recovery speed, and long-term stability. These include $Ba_{0.7}Sr_{0.3}TiO_3$ [41], $Na_2Ti_3O_7$ [42], $Bi_{0.5}K_{0.5}TiO_3$ [43], v-doped nanoporous $Ti_{0.9}Sn_{0.1}O_2$ thin film [44], graphene oxide

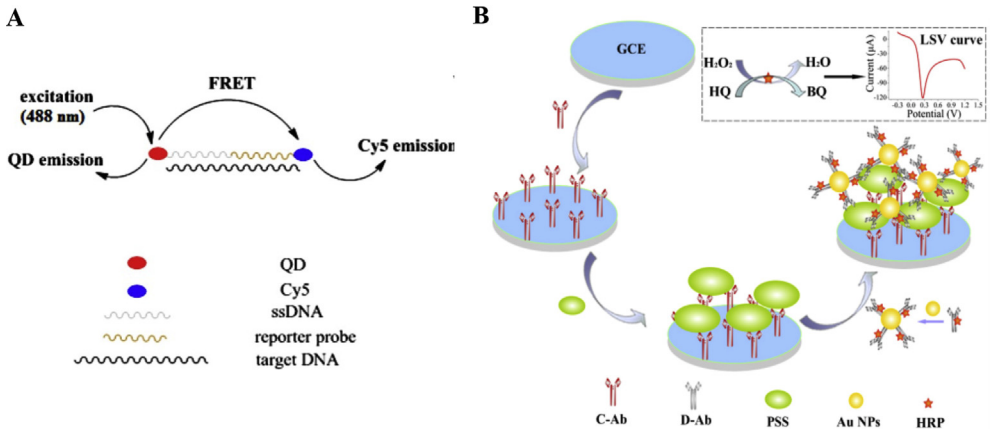

Fig. 3. A) Fluorescence resonance energy transfer between donor QD and acceptor Cy5. B) Schematic Illustration of Au NPs Amplified Electrochemical Immunoassay for PSS Detection.

films [45], $Bi_{0.5}Na_{0.5}TiO_3$—$Bi_{0.5}K_{0.5}TiO_3$ [46], Sr(II)-added $BaAl_2O_4$ composites [47], $Mn_{0.2}Ni_{0.8}Fe_2O_4$ nanoparticles [48].

As an example, $Na_2Ti_3O_7$ nanotubes coated them on Al_2O_3 ceramic substrate were synthesized to fabricate an impedance sensor for humidity using Ag—Pd as interdigitated electrodes, with sensitivity in the range from 11 to 95% relative humidity, a maximum hysteresis less than 3% RH, and a quick response-recovery time (2 and 4 s, respectively) [49].

Graphene oxide films were also exploited as humidity sensing material being able of significantly improving the sensitivity and the response time of sensors. Zhao and colleagues fabricated a humidity sensor by using different graphene oxide films dispersion concentrations, obtaining high sensing capacitance as well as fast response and good repeatability [45].

Optical sensors have similarly exhibited remarkable benefits over their electrical counterpart, being able of working without interference from electric or magnetic fields. The principle is founded on the interaction of the water vapour with the sensitive material that leads to a variation of optical parameters. Many smart materials at the nanoscale have been exploited to develop optical sensors for humidity measurements. A composite material constituted of multi-walled carbon nanotubes and Nafion was deposited by drop-casting on the surface of an acoustic wave resonator providing improved sensitivity and dynamic characteristic due to its large specific area and special ionic conductivity [50]. Indeed, this sensor showed a high sensitivity up to 260 kHz/% RH, good linearity with $R^2 > 0.99$, high precision of 0.3% RH at low humidity level below 10% RH. A graphene oxide film was used to coat a SU8 polymer channel waveguide using by drop-casting technique, obtaining a linear response of 0.553 dB/% RH in the range of 60%–100% RH in less than 1 s [51].

Finally, nanotechnology offers also the advantage to realize miniaturised sensors with advantages as low hysteresis batch fabrication and ease of integration with cost reductions.

3. Future perspectives

Nowadays, progress in nanotechnology based (bio)sensors are sensibly increasing with the aim to provide rapid, sensitive, and cost-effective analysis tailored on farmer requirements. However, at the state of the art on biosensors, several limitations still hamper the wide use of this technology in the real field, including for example the low storage and working stability of the bio-components. To this regard, last trends in biotechnology, biomimetic chemistry, nanotechnology, and material science are nowadays furnishing suitable tools for the design of more robust biological recognition elements by producing artificial molecules able to mimic key properties of natural ones, or tailor them to deliver new custom-made features, as aptamers, molecular imprinting polymers, peptide nucleic acids, and synthetic peptides [52].

In addition, failure in obtaining data about soil characteristics and crop quality in a rapid and inexpensive manner remains one of the biggest limitations of smart agriculture, due to the lack of automated sampling and treatment, taking in special consideration complex matrices as soil. In fact, soil sample treatment is a critical concern because it requires several steps, including sampling, extraction of targets from the samples, and clean-up. Considering the high complexity and the low homogeneity of soil matrix, it is hard to provide an automated extraction tool embedded in the biosensor to deliver standoff analysis. For this reason, further research efforts are required to design biosensor configuration for real application, entailing easy and effective sampling and treatment.

Moreover, the simultaneous detection of both analytes and parameters in water as well as complex matrices as soil and plants should be also a fundamental requisite in smart agriculture. To face this concern, the recent results in material science highlighted the potential of several materials (e.g. silicon, glass, paper, plastic, other polymer) for projecting multiplexed, miniaturised, automated, and integrated (bio)sensors. Among these materials, paper has attracted significant attention in the last years for the development of simple, easily fabricated, disposable, and low cost devices. In addition, the combination of paper with microfluidics provides a mechanism for multiple detection, separating particulates from fluids and avoiding interference among different chemical species [53].

Furthermore, the convergence of cutting-edge technologies including integration in wireless sensor networks for data management [54], 3D printing, internet of things, and solar cells will have a giant impact on nanostructured (bio)sensor progresses for smart agriculture.

4. Conclusions

In the past half century, there has been a notable increment in food production to face the increase of world population, which could reach 8.9 billion by 2050 [55]. To this aim, intensification of agricultural practices has been a prime driver of enhanced food production in the last decades, delivering nowadays an additional 25% of food compared with 1960 [56].

However, there are several claims for rethinking agriculture by developing more environmentally friendly intensification practices able providing food security as well as complying environmental and human safety. These novel practices need to be founded on core principles of sustainability, including the minimisation of the impacts of management systems on biodiversity, greenhouse gas emission, clean water, and spreading of pests and weeds [57–59]. In this context, nano (bio)sensor technology can pave the way for fostering a precision agriculture based on a more sustainable and wise use of the resources (water and land) as well as chemicals (fertiliser and pesticides), with the aim to enhance crop yields while respecting ecosystems. Indeed, in the face of rising pressure from climate change, growing populations, and decreasing crop yields, nanostructured (bio)sensors will have a significant role in the future of food and agriculture, being able to provide continuous and real-time monitoring of critical parameters for enhancing the productivity and ensure compliance with mandatory hygiene and traceability rules.

Nevertheless, despite their astonishing features in terms of high efficiency, ultra-sensitivity, robustness in storage/working conditions, minimal reaction time, accuracy, reproducibility, biocompatibility, portability, and low cost, nanostructured (bio)sensors are still under their infancy. Indeed, the most of them are at a laboratory set-up or have been developed for operating in simpler matrices as water, while there is still a gap between the design of biosensing systems and their effective application in soil analysis. In this perspective, the convergence of cross-cutting disciplines including bioinformatics and rational design of novel artificial bioreceptors (e.g. aptamers, peptide nucleic acids), innovative functional materials (e.g. nanocellulose), microfluidics, 3D printing, and internet of things will have an enormous influence on the development of custom-made nano (bio)sensor at the forefront of a sustainable agriculture.

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